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Gradient composition sol-gel materials

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Abstract

The STARDUST Mission, which launched in February of 1999, plans to fly through the coma of Comet 81P/Wild2, capture some of the material ejected by the comet, and return the samples to Earth in 2006. The capture media for the encounter is silica aerogel. In the course of the capture media development the aerogel evolved from single density, to discontiuous (layered) density changes, to a continuous (gradient) density change. Since various physical properties such as the index of refraction, the porosity, the dielectric constant, etc., are directly related to the density of these materials, they too vary in a gradient manner. Employing the method developed for the production of the STARDUST media, samples have been produced which exhibit order of magnitude density changes and refractive index gradients of up to 0.1. Other samples have been made which include compositional gradients such as varying dopant(s) concentration and oxide composition. The method has been used to form samples that display linear, planar, and cylindrical gradients. Sol-gel materials have been produced of not only gradient aerogel, but also gradient xerogel, as well as, gradient hybrid aerogel/xerogel materials.

Keywords: Sol-gel, Gradient Composition, Aerogel, Xerogel

1. Introduction

The sol-gel method has seen tremendous growth over the past several decades. The literature concerning sol-gel chemistry includes a many articles touting the potential commercial aplications that can be realized with sol-gel derived products. However, to date, few if any sol-gel derived products have seen any commercial success. It is widely accepted that sol-gel products are either too expensive to be competitive or they are impractical due to some factor such as a lack of structural integrity. The latest avenue being perused by sol-gel chemists to make competitive products is the doping sol-gel derived materials with functional moieities, using the aerogel or xerogel as the host matrix. Due to the fact that aerogel and xerogels have physical properties such as high porosities, high surface areas, etc., they lend themselves to this role quite well. Still the functional properties that innately make aerogel and xerogel such attractive candidates for a variety of other roles go unused. Aerogels, in particular, exhibit concurrently a list of physical properties that make them potentially applicable in a variety of areas and yet cost and durability make them less than commercially viable.

Sol-gel processing is sufficiently malleable that it is particularly appealing to material scientists in the production of a wide range of highly porous inorganic oxide and carbon based networks. Sol-gel processing is based on the gelation of polymerizable moieties and the subsequent drying of the porous network formed. The gelation generally arises from the hydrolysis and condensation of a metal alkoxide. However, gels have also been formed from the polymerization of reactive organic and hybrid organic/inorganic species. A number of reviews have been written about the sol-gel process and its many manifestations[1-3] Since there exists such a vast variety of alkoxides and since the resultant material depends on the experimental parameters of the material processing, the scope of materials produced via the sol-gel method are extensive.

The materials produced by the sol-gel method are divided into two general categories, xerogels and aerogels. The gelation stage of the overall process is typically very similar in the both caes. However, xerogels are dried at roughly ambient temperatures and pressures, while aerogels are usually dried under supercritical conditions. Although, various authors have published accounts regarding the production of aerogels and low density xerogels without employing the supercritical solvent extraction method [4-7].

The STARDUST Project assembled two grids containing several hundred aerogel blocks which will be used to capture interstellar and cometary grains during its seven year mission. In the course of developing the capture media aerogel for the mission, both layered density and then gradient density aerogel were manufactured. The formation of the layered density blocks was quite straight forward in that a mixture of sol, solvent, water, and catalyst was poured into a mold and allowed to gel. Other mixtures of slightly different composition were then poured over the existing gel and gelled. Once the final layer had gelled, the sample was then dried via supercritical extraction. A method was then developed that allowed for the production of continuously gradient density aerogel. Various density profiles were produced, qualified for flight, and used in the assembly of the flight article.

Aerogels with gradient density profiles were developed for STARDUST since they are being used as the capture media. An incoming particle would first encounter the "softer", less dense impact face which would act to begin the deceleration process. As the particle traveled further into the aerogel and slowed, it would gradually encounter increasing resistance due to the increasing density of the media. Sol-gel materials with other gradient properties could be used in other applications. Since a number of intensive physical properties correlate to the density, they too are gradient in nature. For example, below are given the equations which relate density (ρ), index of refraction (n), porosity (P), and dieletric constant (k').

Index of Refraction	$n = 0.21\ \rho + 1$	(1)
Porosity	$P = 1 - (\rho/2.19) = [(1.458-n)/0.458]$	(2)
Dielectric Constant	$k' = 1 + 7.7(n-1)$	(3)

If r = 10 mg/cc, then n = 1.003, P = 0.993 and k' = 1.02.
If p = 100mg/cc, then n = 1.024, P = 0.947 and k' = 1.19.

Thus, a material that changes continuously in density from 10 to 100 mg/cc will exhibit a corresponding change in these other properties.

Take, for example, the relationship between the acoustical impedence (Z) of a material and its density. As noted by Fricke, a sol-gel material with gradient density would also have gradient acoustical impedence [8, 9]. The intensity of the sound radiated from one material to another, e. g., a piezo ceramic to air, depends on the values of the acoustical impedence of each of the materials. Since Z is $\sim 10^7 kg/m^2$ sec for the piezo ceramic and $\sim 10^2$ kg/m^2 sec for air, energy is dissipated at the interface. However, if a gradient density material were placed at the interface much of the sound intensity would be retained. Sol-gel materials with density gradients from several hundred mg/cc to tens of mg/cc have a gradient acoustical impedence of $\sim 10^6 kg/m^2$ sec to $\sim 10^3 kg/m^2$ sec. A material such as this would bridge the ceramic to air interface with considerably less intensity loss. Another example is that in which gradient density materials could be used as windows where a continuous transition from glass to aerogel was required.

Control of the density profile then carried over into the localized control of other physical properties within a sol-gel sample. As a result of this development, materials have been produced that incorporated regions of tailored density and thus gradient porosity, refractive indices, dielectric constants and acoustical impedence. The method has also been used to make samples with gradient and localized doping and oxide content.

The applications of GRIN rod lenses are expanding as they are employed in telecommunications and optical imaging. A great deal of work has been spent in the development of gradient index (GRIN) of refraction rod lenses using the sol-gel method [10 - 15]. Ion exchange, ion stuffing, diffusion, hydration and evaporation have all been used to achieve optical gradients. However, these procedures are rather laborious and costly. By employing the techniques developed for STARDUST compositional gradients can be established prior to gelation and thus no post-processing is necessary to form GRIN rod lenses.

2. Experimental

2.1 Materials

Tetraethyl ortho silicate (TEOS, Aldrich Chemicals, 98%) was distilled under nitrogen in quartz distillation ware. Acetonitrile (Aldrich Chemicals, 99.93% HPLC Grade), ethyl alcohol (Quantum

Chemicals, 200 proof), nitric acid (Aldrich Chemicals, 70 %, double distilled), ammonium hydroxide (Aldrich Chemicals, 28% double distilled), tin chloride (AldrichChemicals), resorcinol (VWR, 99%), formaldehyde (VWR, 10%, buffered), sodium carbonate (VWR) were all used as received.

2.2 Procedures

2.2.1 Aerogel

A two-step procedure was used to make the aerogel [16 - 18]. After mixing together the TEOS, ethyl alcohol, water and nitric acid so that it formed a single phase, the mixture was refluxed for several hours and then distilled to remove ethyl alcohol. When a target temperature was reached the distillation was stopped. A second aliquot of TEOS was added and the system was refluxed. When the reflux was complete, a second distillation was conducted to further remove ethyl alcohol from the mixture. When a second target temperature was reached, the distillation was stopped. After allowing the sol to cool, it was diluted with acetonitrile.

The precursors for the wet gels were composed of sol, acetonitrile, water and ammonium hydroxide. After stirring, the mixture was introduced into glass molds. The density of the resultant gels was dictated by the ratios of the four precursor components. To establish a gradient density the ratios were varied across the profile of the sample. Once the wet gels had set, they were dried under supercritical conditions.

2.2.2 Xerogel

Xerogels were produced using both a two-step method and a single-step method. For the two-step method, a sol (as described above) was used as the source of the alkoxide. For the single-step method, TEOS was used as the source of the alkoxide. In each case, the alkoxide was combined with solvent (typically acetonitrile), water and catalyst. After the mixture had gelled, it was dried slowly in a glovebox with an atmosphere that was partially saturated with the solvent employed.

Depending on the compositional gradient desired the mixture varied in alkoxide to solvent content, dopant content, or alkoxide type. As above, the composition of the precursor was varied across the profile of the wet gel, which resulted in a gradient in the dried gel.

2.2.3 Aerogel/Xerogel composites

Aerogel/xerogel composites were produced by forming a wet gel using the two step aerogel procedure. An initial density gradient was established during the formation of the wet gel. The density gradient was then enhanced by partially drying the wet gel to form regions of xerogel and the piece was then dried supercritically.

2.2.4 Gradient oxide and gradient dopant composites

Gradient oxide and gradient dopant composites were produced by using the gradient density aerogel method and varying the alkoxide or the dopant being introduced to the wet gel precursors. The tin oxide aerogel in the mixed oxide samples was produced using the method given by Kistler [19]. The carbon aerogel in composite silica - carbon samples was produced using the method given by Pekala [20].

2.2.5 Refractive index and density measurements

The Gladstone, or Minimum Deviation, Method was used to measure the density profiles of the samples when the geometry of the sample allowed [21]. The Gladstone method is based on the fact that the density and the refractive index are directly dependent. By directing a 632nm He-Ne laser with a line generator through the corner of a sample the beam was bent, see Figure 1. Samples of monolithic density aerogel were made, the density was calculated by determining the mass and size of each piece, and then used to calibrate the method. The density profiles of gradient samples were then measured by recording the deflection of the beam and calculating the corresponding density.

The refractive index profiles of the gradient index of refraction rod lenses were examined with a differential interference microscope. A rod lens xerogel was sectioned lengthwise to obtain a portion suitable for investigation. The intial sample was approximately 2.0 cm in diameter and 2.0 cm in height.

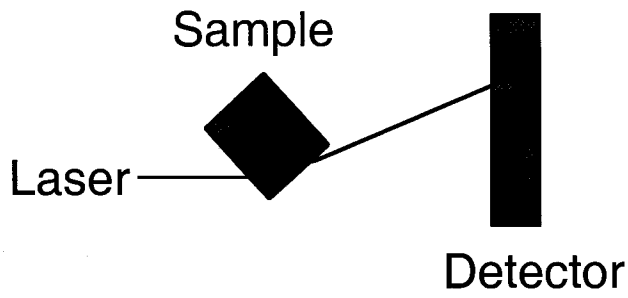

Figure 1 Illustration of set-up for the Gladstone method

3. Results and discussion

3.1 Gradient density

The samples prepared for the STARDUST cometary particle collector were blocks of silica aerogel approximately 4 cm X 2 cm X 3 cm in size.

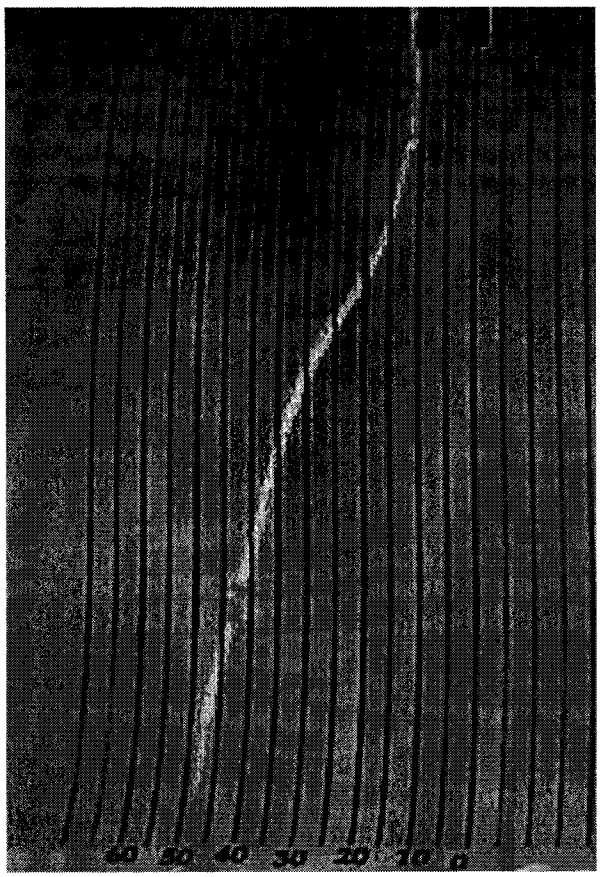

Figure 2 STARDUST cometary particle collector aerogel gradient density profile.

The typical cometary gradient density profile varied from 0.010 g/cc at the particle impact face to 0.050 g/cc at the base. Figure 2 illustrates the change in density across the vertical profile of a cometary sample using the Gladstone method.

Since the method used to generate these gradient density samples involves varying the precursor content across the profile of the sample, the density profile can be tailored. The STARDUST Project is designed to capture particles from a comet and will undoubtedly encounter small, dense particles and larger, aggregated particles. Since the capture properties are different for these different species the density profiles were varied to accommodate the capture of different types of particles. The amount of low and high density aerogel was varied by changing the position of the gradient transition in the profile. The length of the transition was also varied to change steepness of the gradient.

Samples are also being flown in the STARDUST collector which are intended to collect interstellar grains during the flight to the comet. These blocks are approximately 4 cm X 2 cm X 1 cm in size. The nominal density profile varies from 0.010 g/cc at the collector impact face to 0.20 g/cc at the base.

Figure 3 illustrates the density profile across the vertical profile of an interstellar sample of STARDUST aerogel.

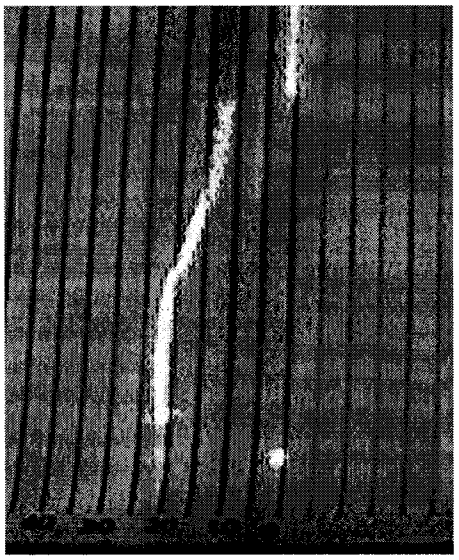

Figure 3 STARDUST interstellar grain collector aerogel gradient density profile.

3.2 Gradient oxide and gradient dopant materials

The method developed for the production of the gradient density silica aerogel for the STARDUST Mission has also been employed to make gradient oxide and gradient dopant materials.

Figure 4 shows a block of silica aerogel that has been gradiently doped with a tin oxide precursor. The composition of the aerogel varies continuously from primarily tin oxide at the base to silica at the upper face. The same technique has been used to add a dopant to a silica wet gel precursor across a vertical profile resulting in a gradiently doped aerogel after drying. A cylindrical sample has been produced which is doped in a gradient manner with a laser dye. In a similar way, blocks of sol-gel material could be doped to enhance their ability to act as luminescent solar concentrators [22]. Concentrators could be produced which incorporated two or more fluorescent moieties in series. Also, the refractive index could be tailored to assist in guiding the light in predetermined directions, i.e., toward a photovoltaic cell.

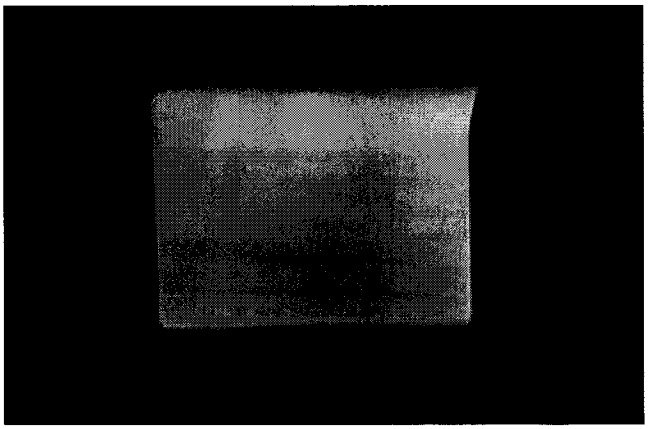

Figure 4 Axial gradient composite oxide aerogel.

Figure 5 shows a disc of silica aerogel that was doped radially with resorcinol-formaldehyde organic gel reagents. The inorganic and organic mixtures gelled concurrently, doping the central region of the final aerogel with carbon.

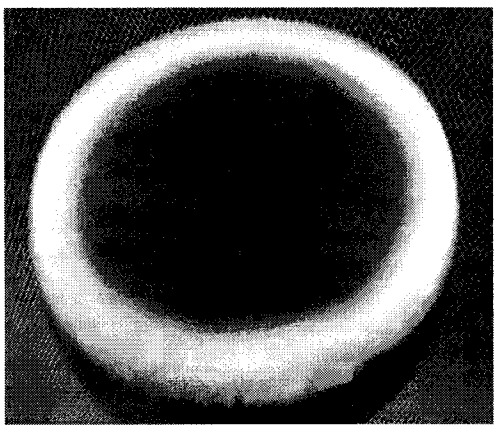

Figure 5 Radial gradient composite silica/carbon aerogel.

The examples illustrated above demonstrate that sol-gel materials can be made that have tailored gradient properties. A commercial application that is of great interest is the use of sol-gel materials as catalysts supports. By using the method outlined here it is possible to dope a precursor wet gel with a series of chemical moieties. It is also possible to selectively dope prescribed regions of a sol-gel material. In this way, a column of aerogel could be selectively doped with a series of catalytic species. The material could then be used for conducting serial chemical reactions.

3.3 Gradient index of refraction - axial

Figure 6 shows an axial gradient density silica sol-gel material that varies from a density 0.500 g/cc to that of 0.050 g/cc. In fact, the change demonstrated is that from a xerogel to an aerogel in a continuous manner. The two-step method was employed to form the xerogel/aerogel sample. An initial density gradient was established prior to the gelation of the sample. After gelation the column was selectively dried under ambient conditions, forming a continuous transition from a xerogel to an aerogel. The sample was then dried supercritically in an autoclave. The density profiles of several axial GRIN cylinders were determined by sectioned them and then weighing and measuring the volume of each section.

The density was also determined using the Gladstone method using the previous results for calibration. The xerogel/aerogel cylinder is pictured between two polarizing filters to demonstrate the change in density which is visualized by the resultant birefringence.

Using this method of fabrication materials that change continuously from high density silica, i.e., xerogel, to very low density silica, i.e., aerogel, can be produced. Materials that change from a glass to an aerogel become possible. Materials such as these could be employed for acoustical impedence matching, as discussed above. They could also be employed as specialty windows, where one environment requires a high density glass while the other requires an ultralow density aerogel. Axially gradient index of refraction optical materials can be used to replace aspheric optics. A spherically shaped axial GRIN lens can be used in the place of an ashperic.

Figure 6 Gradient density xerogel/aerogel composite.

The method for making xerogel/aerogel composites has also been used to form aerogel blocks with selectively dried surfaces which greatly increases their structural integrity and makes them much more durable. Materials with bulk aerogel properties, while having selectively dried rigid surfaces have be made.

This eliminates the need for inserting the aerogel into a frame or some other rigid structure to maintain the structural integrity of the aerogel. Another way to stregthen aeogel materials has been to add fibers to the bulk phase. By creating a xerogel shell on the aerogel, the supportive/protective structure is an integral part of the bulk material and is continuous with it. Xerogel surfaces coating aerogel bulk materials can be used to protect the aerogel from environments that it can not withstand, while presenting a material with bulk aerogel properties. Ultimately, this method makes aerogel a much more practical material for general commercial applications.

3.3 Gradient index of refraction - radial

Figure 7 shows a qualitative illustration of the gradient index of refraction of the rod lens formed. The gradient index rod lens was placed on a lirror and a He-Ne laser with a line generator was directed through the setup. Since the optical desnity was greatest for the light passing through the central, high density region that protion of the beam was refracted the greated. Two reference lines can be seen to either side of the refracted portion of the beam in the center.

Figure 8 shows the index of refraction profile of a gradient index of refraction xerogel rod lens as observed with an interference microscope. The profile is seen to be slightly asymmetric. Figure 9 shows an illustration of a typical index of refraction profile obtained using the gradient composition method given here.

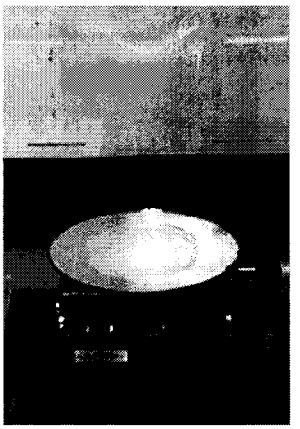

Figure 7 Demonstration of gradient index of refraction.

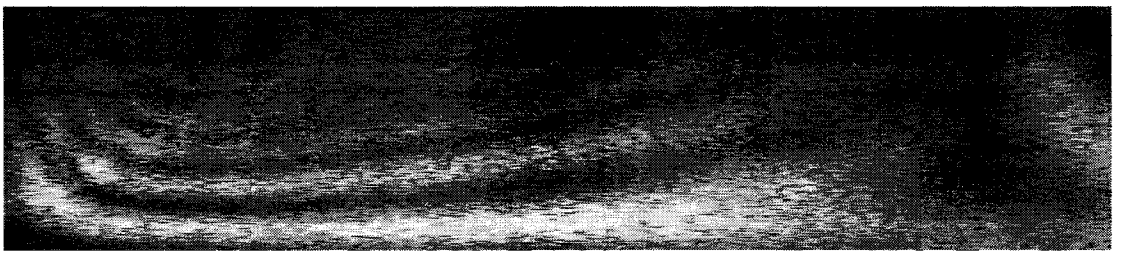

Figure 8 Interferogram of a GRIN rod lens using an interference microscope.

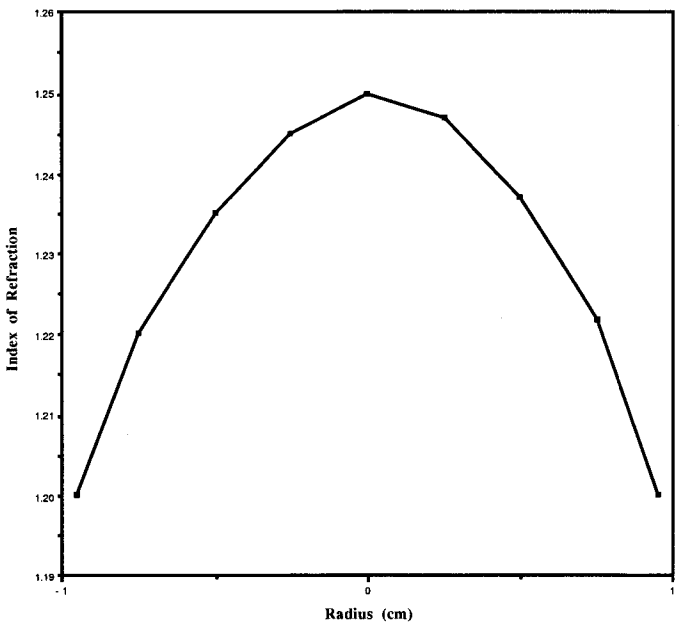

Figure 9 Index of refraction profile of a gradient rod lens

The methods used to make radial GRIN sol-gel materials typically involves either ion exchange or ion stuffing. Solvent exchange, solute leaching and addition are laborious procedures as evidenced by the patents issued regarding these processes [23,, 24]. The rod lenses fabricated and tested for this study were entirely silicon dioxide. The resultant gradinet index of refraction arising from the density gradient that was established prior to drying. The same method is being tested to demonstrate that an oxide gradient, e. g., silicon dioxide and titanium dioxide, could also be established in a cylindrical preform. The presence of both a density gradient and a correlated oxide gradient would greatly increase the optical gradient

Conclusion

The method developed to produce gradient density sol-gel materials can be employed to produce materials that have other gradient properties, such as, gradient dopant composition, gradient oxide composition, etc. Attempts to make aerogel commercially viable has been ongoing for decades with little success. The aerogels being promoted for commercialization are undifferentiated and thus possess functionalities that are uniform throughout the material. A gradient composition material, on the other hand, allows one to locally tailor the physical values of its properties, i. e., the functionality, to suit the needs demanded by a given application. Within a single aerogel cell one can design the properties of the material to vary from low to high and back to low, if needed, in three dimensions. Light, heat and sound can be directed through the material along specified avenues. Different chemical reactions can be catalyzed in preselected areas of a single cell. Specialized windows can be produced that change continuously from one type of material to another as dictated by the two different environments encountered. By creating materials that display these types of controlled, localized functionalities, aerogel technology can be raised to the level at which commercialization becomes realizable.

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References

1. C.J. Brinker and G. W. Scherer, *Sol-Gel Science; The Physics and Chemistry of Sol-Gel Processing*, Academic Press, NewYork, 1990.
2. J.Livage and C. Sanchez, " Sol-gel chemistry", *J. Non-Crystalline Solids* **145**, pp. 11 - 19, 1990.
3. L.L. Hench and J. K. West, "The sol-gel process", *Chem. Rev.* **90(1),** pp. 33 - 72, 1990.
4. R. Kocklenberg, B. Mathieu, S. Blacher, R. Pirard, J. P. Pirard, R. Sobry and G. Van den Bossche, "Texture control of freeze-dried resorcinol - formaldehyde gels", *J. Non-Crystalline Solids* **225**, pp. 8 - 13, 1998.
5. S. S. Prakash, C. J. Brinker, A. J. Hurd and S. M. Rao, "Silica aerogel films prepared at ambient pressure by using surface derivatization to induce reversible drying shrinkage", *Nature* **374**, pp. 439 - 443, 1995.
6. S. S. Prakash, C. J. Brinker and A. J. Hurd, "Silica aerogel films at ambient pressures", *J. Non-Crystalline Solids* **190**, pp. 264 - 275, 1995.
7. D. M. Smith, D. Stein, J. M. Anderson and W. Ackerman, "Preparation of low-density xerogels at ambient pressure", *J. Non-Crystalline Solids* **186**, pp. 104 - 112, 1995.
8. R. Gerlach, O. Kraus, J. Fricke, P.-Ch. Eccardt, N. Kroemer and V. Magori,"Modified SiO2 aerogels as acoustic impedence matching layers in ultrasonic devices", *J. Non-Crystalline Solids* **145**, pp. 227 - 232, 1992.
9. J. Fricke and A. Emmerling, "Aerogels", *J. Am. Ceram. Soc.* **75(8),** pp. 2027 - 2036, 1992.
10.M. Yamane, J. B. Caldwell and D. T. Moore, "Preparation of gradient - index glass rods by the sol-gel process", *Mat. Res. Soc. Proc.* Vol. 73, pp. 765 - 767, Mat. Res. Soc. Pittsburgh, 1986.
11. M. Yamane, A. Yasumori, M. Iwasaki and K. Hayashi, "GRIN rod of large diameter and large delta-N", *Mat. Res. Soc. Proc.* Vol. 180, pp. 717 - 725, Mat. Res. Soc., Pittsburgh, 1990.
12. K. Shingyouchi and S. Konishi, "Gradient - index silica rod lenses produced by a solgel method", *Applied Optics* **29(28),** pp. 4061 - 4063, 1990.
13. K. Shingyouchi, S. Konishi, K. Susa and I. Matsuyama, "Radial gradient refractive - index glass rods prepared by a sol-gel method", *Elect. Letts.* **22(2),** pp. 99 - 100, 1986.

14. K. Shingyouchi, S. Konishi, K. Susa and I. Matsuyama, "r-GRIN TiO2 - SiO2 glass rods prepared by a sol-gel method", *Elect. Letts.* **22(21)**, pp. 1108 - 1110, 1986.
15. S. Konishi, K. Shingyouchi and A. Matishima, "r - GRIN rods prepared by a sol-gel method", *J. Non-Crystalline Solids* **100**, pp. 511 - 513, 1988.
16. T. M. Tillotson, L. W. Hrubesh and I. M. Thomas, Better Ceramics Through Chemistry III, eds. C. J. Brinker, D. E. Clark and D. R. Ulrich, , Mat. Res. Soc. Proc. Vol. 121, ff. 685, Mater. Res. Soc., Pittsburgh, 1988.
17. T. M. Tillotson and L. W. Hrubesh, Better Ceramics Through Chemistry IV, ed. B. J. J. Zelinski, C. J. Brinker, D. E. Clark and D. R. Ulrich, Mater. Res. Soc. Proc. Vol. 180, ff. 309, Mat. Res. Soc., Pittsburgh, 1990.
18. T. M. Tillotson and L. W. Hrubesh, "Transparent ultra-low density silica aerogels prepared by a two-step procvess", *J. Non-Crystalline Solids* **145**, pp. 44 -50, 1992.
19. S. S. Kistler, "Method of producing aerogels", US Patent 2, 093, 454.
20. R. W. Pekala, "Organic aerogels from the polycondensation of resorcinol with formaldehyde", *J. Mat. Sci.* **24**, pp. 3221 - 3226, 1989.
21. W. R. Phillips, *Mineral Optics: Principles and Techniques*, Chapter 3, pp. 47 - 68, W. H. Freeman & Co., San Francisco, 1971.
22. R. Reisfeld, "Spectroscopy and applications of molecules in glasses", *J. Non-Crystalline Solids* **121**, pp. 254 - 266, 1990.
23. S. Noda, "Process for producing a gradient index optical element", US Patent 5, 476, 797.
24. H. Koike and Y. Morita, "Process for making gradient index optical elements", US Patent 5, 837, 023.